PROCEEDINGS OF THE INTERNATIONAL CONFERENCE NANOMATERIALS: APPLICATIONS AND PROPERTIES
Vol. **2** No 1, 01NTF18(4pp) (2013)

The Role of Submonolayer Film Structure in the Surface Diffusion on Atomic Anisotropic Crystal Face: a Computer Experiment

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(Received 07 July 2013; revised manuscript received 14 July 2013; published online 1 September 2013)

We investigated the role of co-operative and structural effects in surface diffusion of adsorbed atoms with repulsive lateral interactions on the atomic anisotropic metal faces by computer simulation method. Such systems were been considered for which chain superstructures can be formed in submonolayer adsorbed films. It is shown that the diffusion coefficients D decrease rapidly with increasing coverage and island sizes in those concentration ranges where first order phase transitions take place. The dependence of D on concentration θ is pronounced very weakly in disordered films at temperatures above the critical one. Due to a crowdion mechanism, the diffusion coefficients are rising as the coverage increases in a homogeneous film in the presence of chain superstructure. Chains commence to change often their positions in the range of critical temperatures. In such conditions, crowdion (quasi-point) configurations of adatoms can associate into soliton-like (quasi-line) formations. The simulation results are compared with experimental data.

Keywords: Superstructure, Surface Diffusion, Phase Transitions, Cooperative Effect, Soliton, Crowdion.

PACS numbers: 68.35.Rh, 68.43.Jk

1. INTRODUCTION

Diffusion plays an important role in the natural processes and in many technologies. In the case of two-dimensional diffusion, the main physical interest in the phenomenon is that the particles in the diffusion process interact with each other and the substrate by intricate way. This leads to a pronounced collective character of diffusion, sometimes with very specific mechanisms. The adsorbed atoms can form a large number of ordered structures. Their symmetry and physical characteristics depend on the properties of the particles as well as the structure and characteristics of the substrate, which accordingly affects the kinetics and diffusion mechanisms. The role of surface diffusion increases particularly at the transition to the nanometer dimensions of objects. So, the corresponding rapid changes in nanoscale objects realized through diffusion (and they are both desirable and undesirable) can strongly modify their properties.

2. RESEARCH METHODS

The aim of the study was to investigate using mathematical simulation the role of cooperative and structural effects in surface diffusion of adsorbed atoms with dipole-dipole interaction on the faces of the atomic anisotropic metals.

Real adsorption systems Li-W(112) and Li-Mo(112) were selected as a prototypes for development of the model performed with the use of molecular dynamics. In our experimental studies [1, 2] carried out using a contact-potential scanning microscope, it was found that the phase state of the adsorbed film greatly affects the kinetics of surface diffusion. The fact is, undoubtedly, a manifestation of the cooperative effects in the diffusion of adatoms in submonolayer films. A series of working hypotheses about the mechanisms of diffusion in phase-inhomogeneous films and self-organization processes of diffusion zone was formulated on the basis of experimental data. However, the applied experimental method did not allow studying the surface diffusion at the atomic level. In this study, we attempted to test the hypotheses proposed early by using computer experiment and obtain new results.

Investigated by us adsorption systems have sufficiently simple phase diagrams in the range of coverages $\theta \le 0.5$ [3, 4]. Chain structures oriented perpendicular to the substrate grooves, i.e. in the direction [110], are formed with the growth of the coverage θ. Then the islands of structure $p(1 \times 4)$ arise. When coverage amounts to $\theta_{Li} \approx 0.25$, the islands of structure p(1×2) are formed on the background of phase p(1×4). The coexistence of two different phases is a feature of a first order phase transition. Lithium forms structure p(1×3) on tungsten as well [3]. If $\theta_{Li} > 0.5$, than the adsorbed submonolayer film loses a structural compliance with the substrate along the crystallographic direction [111], becomes incoherent. Only at $\theta_{Li} = 1$, atoms occupy coherently all adsorption sites again.

On choosing a model of the adsorbed film, which corresponds to real systems Li-Mo(112) or Li-W(112) at $\theta_{Li} < 0.5$, we made some assumptions. The potential of the lateral interaction of adatoms was chosen close to the values obtained in the experimental works [1, 2] at $\theta_{Li} = 0.25$. It was believed that the potentials are independent on the coverage degree and appropriate overlap only, forming a local mean field with which given atom interacts. Recall that lithium is electropositive relatively to tungsten and molybdenum. According to our experimental estimates, the values of the dipole moments of the lithium are close to 1.6 Debye on tungsten and to 1.4 Debye on molybdenum at low coverage degrees. An indirect interaction of adatoms via an electron

gas of the substrate is very important. It is strongly anisotropic on (112) faces of tungsten and molybdenum and causes the formation of long-range chain structures p(1×n) [5]. The investigation of chain (striped) structures in strongly anisotropic adsorption systems with repulsive lateral interaction begun a long time ago, but recently attention of researchers to manifestations of self-organization in adsorbed films and their role in various processes on the surface permanently grows [6–9].

3. EXPERIMENTAL RESULTS AND DISCUSSION

We investigated the kinetics of surface diffusion and phase transitions in submonolayer films with structure p(1×4) on atomic anisotropic face of bcc-crystal at $\theta_{Li} = 0.25$ in [1, 2]. Now we expand the scope of our researches up to the concentration range $\theta_{Li} \le 0.5$. Figure 1 shows forms of existence p(1×4) and p(1×2) structures at temperatures below critical one for p(1×4) which we found by calculations. As you can see, there are two concentration regions of existence of first order phase transitions where submonolayer film becomes heterogeneous ($\theta < 0.15$ i $0.25 < \theta < 0.5$). They are separated by a zone within which the film remains homogeneous with structure p(1×4), but it may have a considerable number of vacancies. The structures and character of phase transitions are in a good agreement with results obtained in [4] for the real adsorption system Li-Mo(112) by Low Energy Electron Diffraction (LEED) method. Therefore, it can be argued that in spite of proximity of used model it reproduces well not only the real structures but the nature of phase transitions. The first order phase transition was found by authors [4] by LEED method already at $\theta_{Li} = 0.07$. In our experiments, separate chain fragments appear initially on the background of two-dimensional gas which begin to coalesce into the islands of structure p(1×4) with increasing coverage (Fig. 1a). The islands of condensed phase disappear only at $\theta_{Li} \approx 0.15$ and the film becomes homogeneous. The film retains the structure p(1×4) in general but contains a large number of vacancies in the chains (Fig. 1b). A quantity of defects in a homogeneous film is reduced with increasing coverage and vacancies in the chains almost disappear at $\theta_{Li} \approx 0.25$ and sufficiently low temperatures.

Chains of adatoms are sufficiently stable formations. If an adatom belongs to chain or its fragment, then it is localized enough steadily on the crystal surface. Being in chain, adatom can fluctuatively shifts along substrate groove by one lattice cell forming a kink. At temperatures below the critical one, adatom sometimes gets the energy required to detach from the chain and to transit into the interchain configurations. In such a way, crowdions – "quasi-point" internode configurations – are formed. The crowdion displaces mainly in the direction of a lower potential barrier (along the substrate grooves) on the atomic anisotropic face but sometimes adatom movements across the grooves are observed too.

The crowdion diffusion mechanism is effective in homogeneous film but it loses the effectiveness drastically when the film transits to a heterogeneous state as Fig. 2 shows.

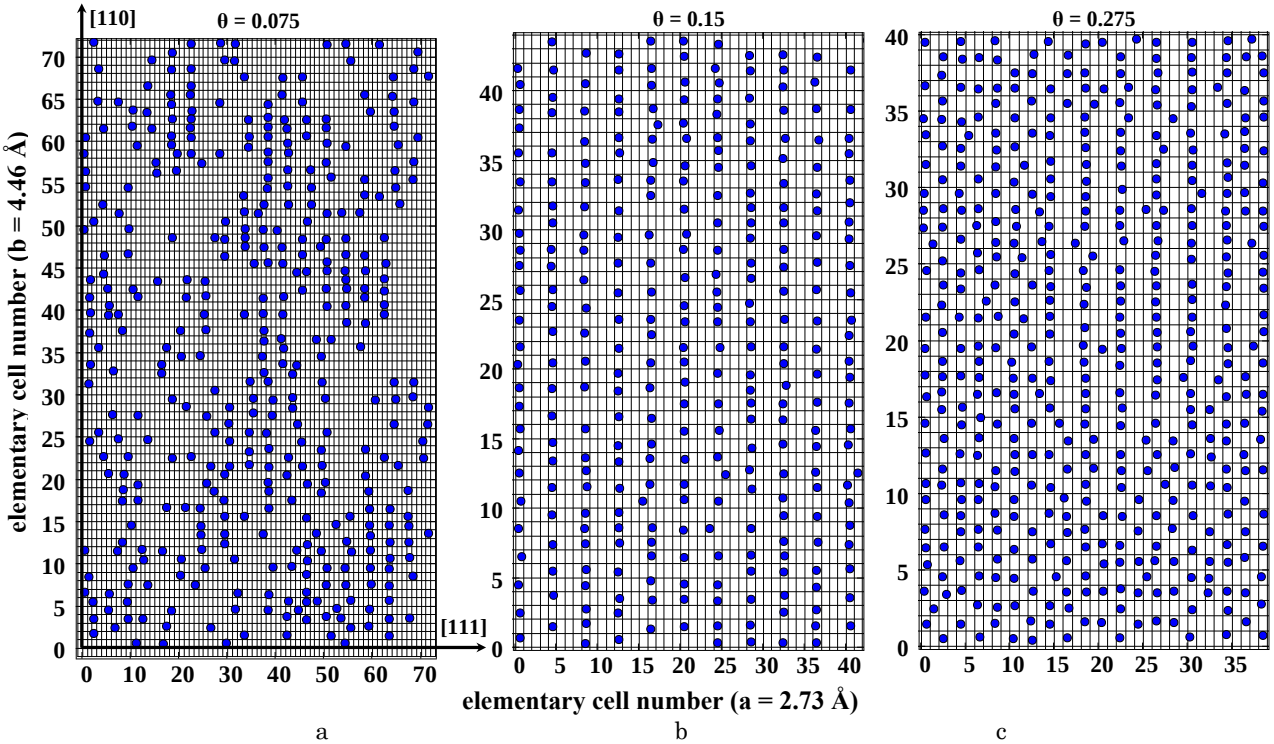


Fig. 1 – Three main types of structures of the adsorbed layer found by simulation at $\theta < 0.5$ and T=145 K. The adlayer is heterogeneous at $\theta < 0.15$ (on the left), is homogeneous at $0.15 \le \theta \le 0.25$ (in the center), and becomes heterogeneous again within the region $0.25 < \theta < 0.5$ where structures p(1×4) and p(1×2) coexist (on the right)

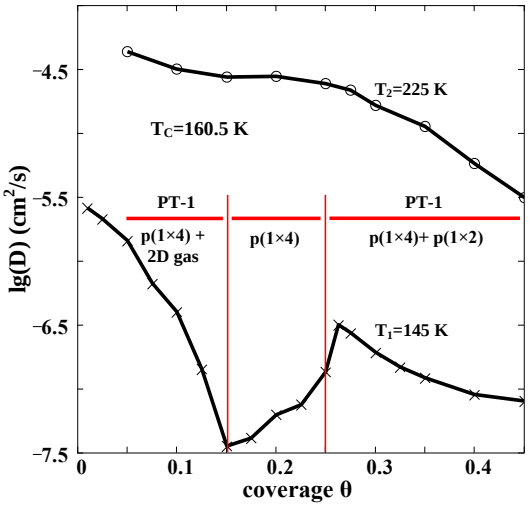
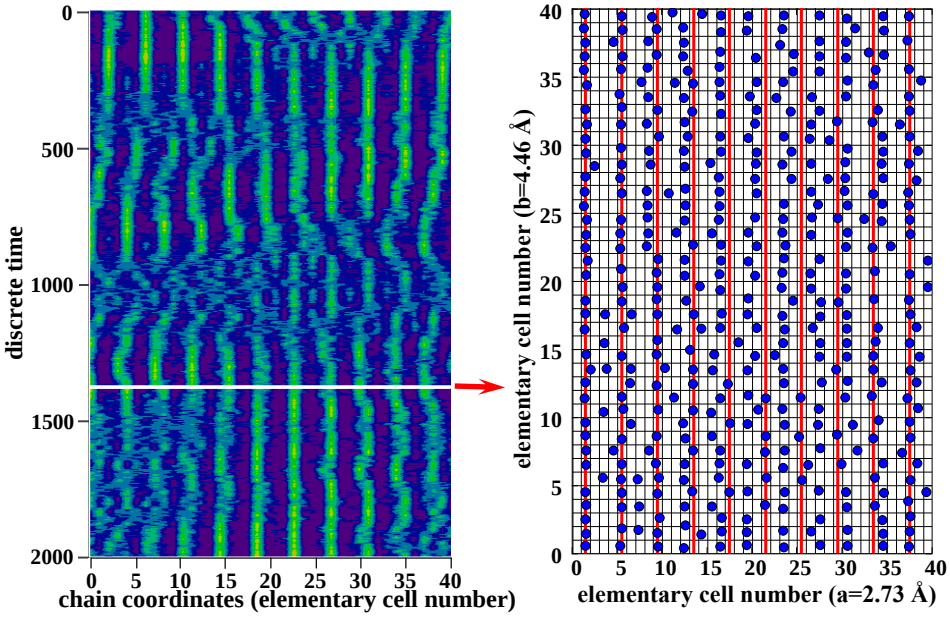


Fig. 2 – Calculated concentration dependences of the diffusion coefficients at temperatures $T_1 < T_C$ i $T_2 > T_C$, where Tc=160.5 K is the critical temperature found for structure p(1×4). The films becomes heterogeneous at temperature T_2 and coverage $\theta_{Li} \approx 0.3$: there are islands of structure p(1×2) on the background of a lattice gas. The profile of the phase diagram is shown at $T < T_C$

The transition of the film from one phase state to another is accompanied by the formation of two sharp peaks at temperatures below critical one, as it is seen on graphs showing the dependence of lgD(θ). Note, that maxima of D(θ) is observed at low temperatures and coverages $\theta \approx 0.27$, that a little exceed the value of stochiometric coverage for structure p(1×4). However, adatoms chains begin to move intensively and contain a large number of vacancies at the critical temperature and slightly above one (Fig. 3). The number of adatoms, which broke away from the chains and left vacancies there, is sufficient for the emergence of islands of new phase p(1×2) on a background of twice rare structure p(1×4). There are two reasons of their appearance. First, with increasing coverage, the diffusion coefficients fast reduce in ranges of first order phase transitions. This is related to concentration ranges $0.07 \le \theta \le 0.15$ and $0.25 \le \theta \le 0.5$. Second, existence of homogeneous structure p(1×4) in range $0.15 \le \theta \le 0.25$ is favorable to realization of such collective diffusion mechanisms as crowdion or even soliton one as it is shown on Fig. 3.



a b

Fig. 3 – The left figure (a) shows how averaged coordinates of the chains change with time. The density of adsorbed atoms in the chain is represented by the intensity of color. The information taken from 2000 frames, distant from each other by 2000 iterations, is given. The white line marks the time coordinate for the 1380-th frame shown in the right figure (b). Notice the appearance and disappearance of the new (eleventh) chain in the left figure. This indicates that the crowdion configurations combine themselves into dynamic soliton-like formations, visible in the right figure, which fluctuatively arise and disappear

Vertical lines in the right figure represent chain locations when the structure p(1×4) arises. However, many vacancies and inter-chain atoms are generated in the structure at stoichiometric coverage $\theta = 0.25$ and temperature close to critical one. Due to these atoms domain wall (soliton) is formed which breaks a periodicity of the structure.

4. CONCLUSIONS

Structuring of the adsorbed submonolayer film strongly influences the character of the surface diffusion. The diffusion coefficients are strongly reduced in the concentration ranges of first order phase transitions with increasing degree of coverage. The fact is related to necessity for adatoms to break away from islands before their displacement in the film. At temperatures above the critical one, the diffusion coefficients are weakly depend on the concentration and monotonically decrease with increasing size of two-dimensional islands in a homogeneous film with no regular structures.

If the structure of a homogeneous film remains unchanged with the concentration, the diffusion coefficients can grow due to increasing efficiency of crowdion diffusion mechanism. In the range of critical temperatures, chain structure becomes floating, that is, the chains begin to frequently change their coordinates and film state reminds liquid crystal in which position order is absent but orientation one remains. The effect can be used to determine the critical temperature. In such circumstances, crowdion configurations of adatoms can be combined into soliton-like formations that have high mobility in submonolayer adsorbed film.

ACKNOWLEDGEMENTS

We thank Academician of the National Academy of Sciences Naumovets A.G. for valuable comments to the manuscript and fruitful discussion and Sryzheus D.V. for program realization of our mathematical model.

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